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Ionic Diodes Based on Regenerated α -Cellulose Films Deposited Asymmetrically onto a Microhole

Barak D. B. Aaronson ^[a], Daping He ^[a], Elena Madrid ^[a], Marcus A. Johns ^[a], Janet L. Scott ^[a], Lian Fan ^[b], James Doughty ^[b], Marco A.S. Kadowaki ^[c], Igor Polikarpov ^[c], Neil B. McKeown ^[d], and Frank Marken ^{*[a]}

Abstract: Cellulose films of approximately 5 μm thickness, reconstituted from ionic liquid media onto a poly-ethylene-terephthalate (PET) film with a 5, 10, 20, or 40 μm diameter microhole, show current rectification when immersed in aqueous NaCl. For “asymmetric cellulose deposits” this rectification, or ionic diode behaviour, is then investigated as a function of ionic strength and microhole diameter. Future applications are envisaged in sustainable cellulose-based desalination, sensing, or energy harvesting processes.

Sustainable microporous materials are of interest in a wide range of applications including gas separation, storage, and water purification. New types of microporous materials have emerged, for example, based on metal-organic frameworks (MOFs),^[1] or based on polymers of intrinsic microporosity (PIMs).^[2] These new types of materials offer opportunities for new technologies to emerge and both MOF^[3] and PIM^[4] materials, in contact to aqueous electrolytes, have been observed to allow nanofluidic current rectification, or “ionic diode” phenomena to occur. Interest in ionic diode devices originates from efforts to mimic natural nanopores^[5] and the development of single channel nanofluidics^[6] with potential for applications in desalination,^[7] energy harvesting,^[8] and in “iontronics”.^[9]

Many natural materials possess microporosity and it is important to ask whether purely natural resources could be employed in the development of new technologies. Cellulose^[10] has been employed in natural and reconstituted

forms for many types of applications. As a natural microporous material cellulose from cotton, for example, offers many benefits in fabrics. Dissolution of cellulose followed by reconstitution^[11,12] is commonly applied to further broaden the range of applications to give improved fabrics, non-woven textiles,^[13] and novel membrane materials.^[14] It is shown here that instead of highly specialised synthetic polymer materials thin films of reconstituted cellulose can be employed in ionic current rectification (or in “ionic diodes”) with potential for future optimisation and applications in desalination or ion separation/detection. Recently, Wei Zhang et al. have demonstrated that a junction between two differently chemically modified cellulose materials can exhibit current rectification.^[15] Here, we use only a single material and the device asymmetry is introduced by deposition onto an inert microhole.

Ionic diode behaviour has been suggested to mimic biological processes^[16] as well as to offer a physical basis for devices for water purification, molecular detection, and energy storage and harvesting. Ionic diode devices generally require asymmetry of charge carrier mobility, which can be achieved in single channel nanopores with chemical modification by employing cone-shaped pores,^[17] at polyelectrolyte junctions,^[18] and electrolyte - ionomer-membranes - electrolyte junctions⁷ with asymmetry in the interfacial contact zone. Recently, we have reported on the ionic diode effects utilizing the asymmetric deposition of polymers of intrinsic microporosity (PIM) membranes using a molecularly rigid Tröger base polymer (PIM-EA-TB).^[19] In these cases the combination of a macroscopic asymmetry in film deposition, as well as the charge distribution and microscopic pore structure, were suggested to lead to ionic diode behaviour. In addition to identifying the key factors contributing to the observed ionic diode behaviour and utilizing them in future applications, there is a need to find sustainable materials with low toxicity and bio-compatibility. Cellulose (Figure 1) appears to offer very attractive properties to be employed as an “ionic diode” component. Although not charged in the crystalline form, cellulose is known to possess negative surface charges due to surface dipoles and inherent carboxylate functionality.^[20] These surface charges can be enhanced or inverted at will when chemical modification methods are applied. However, here we explore α -cellulose without further modification.

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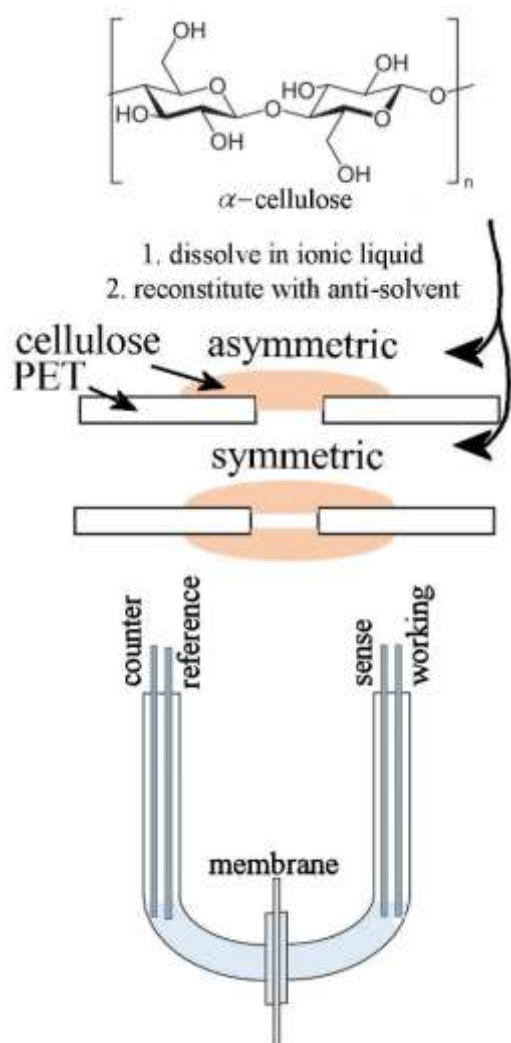


Figure 1. Molecular structure of cellulose and fabrication steps for asymmetric, or symmetric, cellulose films on poly-ethylene-terephthalate (PET) with microhole. Also shown in the 4-electrode measurement cell with working electrode on the side of the cellulose deposit.

Cellulose (Figure 1) is abundant, non-toxic, and readily processible and therefore gaining increasing attention as an alternative to petroleum-based materials. Regenerated cellulose^[14] is generally suggested to assume the form of cellulose II, which has a lower crystallinity index when compared to the native form.^[21] Studies on regenerated cellulose from the mixture of ionic liquid: 1-ethyl-3-methyl imidazolium acetate with dimethyl sulfoxide ([EMIm][OAc] : DMSO) have shown that a lower crystallinity index (or more amorphous) structure of cellulose is formed when alcohols are used as an anti-solvent.^[22] Moreover, the drying of the cellulose was shown to influence the pore size and distribution starting from a bi-modal distribution of pore sizes

consisting of several nm (< 10 nm) each to a mono-modal distribution of pores in the range < 5 nm upon drying.^[23] Cellulose is therefore an attractive material to use as a membrane with controllable pore and charge distribution properties in applications in filters, where pore size and charge control are required, as well as ease of processing.

In this contribution we report on ionic-diode behaviour for asymmetrically deposited cellulose film reconstituted from a mixture of ionic liquid and dimethyl sulfoxide (DMSO) as solvent on a poly-ethylene-terephthalate (PET) support film with a typically 20 μm diameter microhole. Both “asymmetrically” and “symmetrically” deposited films (Figure 1) are investigated. Rectification of currents was observed when immersed in aqueous NaCl solutions on both sides of the asymmetric cellulose membrane (see Figure 1) suggesting that the membrane can be improved for future use in a device, for example in water desalination.

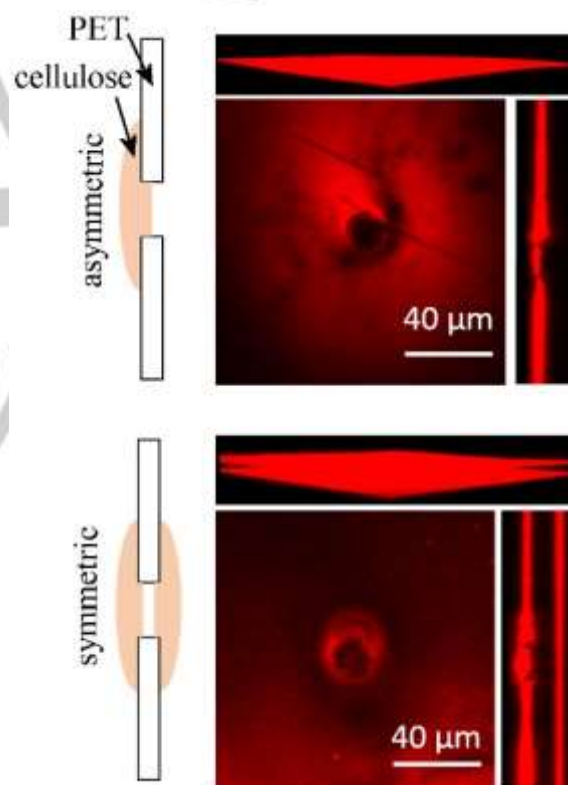


Figure 2. Fluorescence images for an asymmetric (one-sided) and symmetric (two-sided) cellulose film deposit (rhodamine B stained) on a 6 μm thick PET film with 20 μm microhole.

Film Formation. Cellulose films were formed by reconstitution from ionic liquid solution. The drying conditions for the regenerated cellulose proved important. Wet cellulose without drying showed less rectification possibly due to known decrease in pore size upon drying. In order to

characterize the regenerated cellulose films, a solution of rhodamine B was used to provide a positively charged stain on the negatively charged regenerated cellulose films on PET substrates and fluorescence imaging was performed (Figure 2). In the case of asymmetric deposition (cellulose deposited only on one side of the PET membrane) a thin layer of cellulose is observed with little or no cellulose entering the cavity of the laser-drilled 20 μm microhole. When symmetrically deposited, cellulose can be observed on both sides of the PET substrate, although the penetration of cellulose into the microhole cavity cannot be confirmed by fluorescence. It is likely that some cellulose enters the microhole in particular for larger diameter holes (*vide infra*).

Symmetrically and asymmetrically deposited cellulose membranes. To estimate the resistance of cellulose at the location of the microhole, cyclic voltammograms were recorded in aqueous NaCl for a cellulose membrane deposited symmetrically onto the 20 μm microhole and compared for different ionic strengths (Figure 3). The current voltage relationship, in the potential range from -1 V to +1 V, is close to linear for all concentrations, which suggests that the symmetric cellulose membrane is acting like a resistor. The resistance of the electrolyte-filled microhole can be estimated based on equation 1 taking into account the cylindrical microhole and access at both sides.^[24]

$$R = \frac{1}{\kappa} \left(\frac{1}{4r} + \frac{L}{\pi r^2} + \frac{1}{4r} \right) \quad (1)$$

In this equation the microhole resistance R is given by the microhole radius, r , the microhole length, L , and the specific conductivity of the electrolyte, κ (for NaCl^[25] at 25 °C and assuming 0.1 M concentration $\kappa = 1.06 \text{ } \Omega^{-1}\text{m}^{-1}$). The calculated microhole resistance based on equation 1 is in good agreement with values obtained from data in Figure 3A, which suggests that the microhole is filled with electrolyte and ionic current is unimpeded, at least at higher salt concentration.

Perhaps interestingly, in the case of an asymmetrical deposition of cellulose around the PET microhole and for lower concentrations of NaCl, current rectification is observed, as shown in Figure 3B. The rectification ratio (here obtained by dividing absolute currents at +1 V and at -1 V) can be employed as an approximate measure of the rectification efficiency. With increase in ionic strength a clear decrease in rectification ratio is observed consistent with data for other types of porous materials. For application in sea water (ca. 0.5 M NaCl) the porosity and charge density in the cellulose ion conductor need to be further improved.

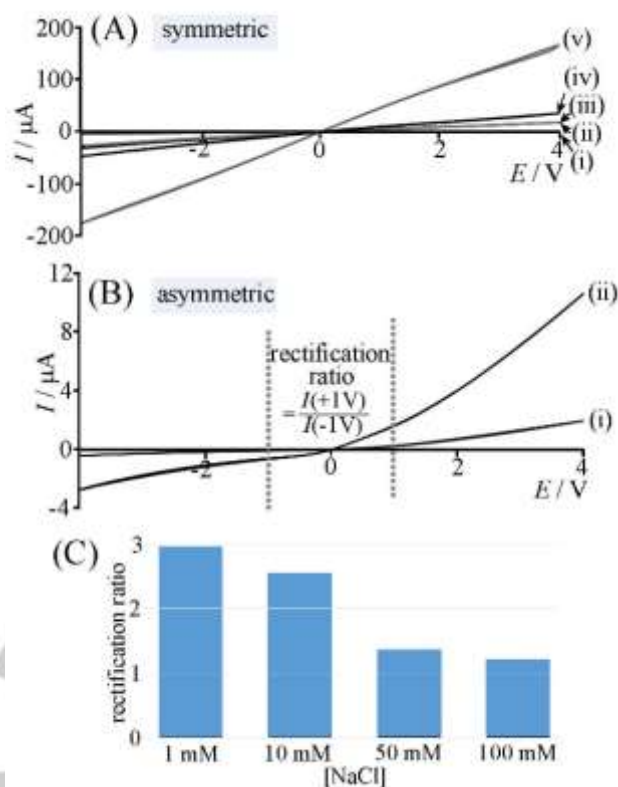


Figure 3. Cyclic voltammetry (scan rate 20 mVs⁻¹) for (A) symmetrically and (B) asymmetrically deposited cellulose membranes in aqueous (i) 1, (ii) 10, (iii) 50, (iv) 100, (v) 500 mM NaCl. (C) Bar plot of rectification ratio as a function of NaCl concentration.

The diode mechanism at the cellulose | aqueous electrolyte interface responsible for the ionic current rectification can be understood in terms of a model developed by Yossifon and coworkers.^[26,27] At the ion conductor | aqueous electrolyte interface both space charge layer formation (within the ion conductor) and/or concentration polarisation (within the aqueous electrolyte) are possible under “closed diode” conditions (here at the small interface within the microhole). At higher applied potential also convective flow phenomena have been suggested to occur. In contrast, for the “open diode” predominantly the resistivity of the ion conductor in and around the microhole are limiting the ion flow. This can be observed in data in Figure 3Ai and 3Bi where similar currents flow in the open diode case, but current is blocked in the closed diode case. The increase in ionic strength weakens concentration polarisation effects and thereby gradually opens the diode. Improvements in the ion conductor (here cellulose) material will allow rectification phenomena to be improved.

The rectification effect is studied next as a function of PET microhole diameter (Figure 4). Values improve from about 2 to close to 4 when going from a 5 μm diameter microhole to

40 μm diameter microhole. This effect seems relatively small and is believed here to be associated with a combination of effects related to microhole geometry.

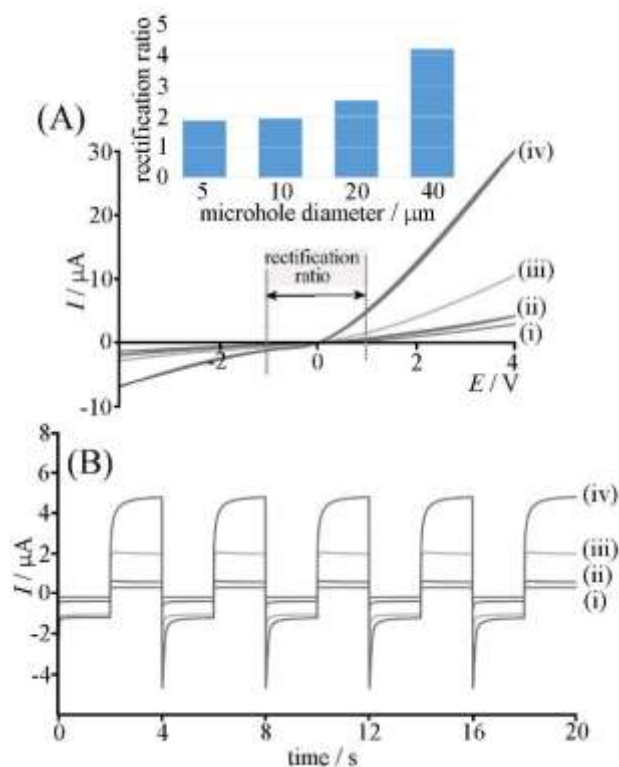


Figure 4. (A) Cyclic voltammetry (scan rate 20 mVs^{-1}) for an asymmetrically deposited cellulose membrane on a (i) 5, (ii) 10, (iii) 20, and (iv) 40 μm diameter microhole. Inset shows rectification ratio at ± 1 V. (B) chronoamperometry data for potential steps from -1 V to +1 V.

For applications in desalination, or ion separation, the rectification effect needs to be improved, which should be possible by (i) further optimisation of the geometry and, more importantly, (ii) by improvements in the pore size and charge distribution in the cellulose material. Work on single channel ionic diodes^[28] has progressed substantially and both device design (based on geometric parameters and charge distribution^[29]) and theory (based on accumulation-depletion models at Nernst-Planck-Poisson level^[30]) have been investigated. Cellulose as a “multi-channel” ionic diode case will require more study and optimisation. It seems likely that both chemical modification of the cellulose and modification of the porosity and cellulose | electrolyte interface geometry will allow for substantial improvements and device development.

In addition to the rectification ratio, the switching time of the ionic diode is of interest. Figure 4B shows chronoamperometry data for repeated switching of the cellulose

diode between applied potentials of -1 V and +1 V. Data are shown for ionic diodes based on PET microholes with 5, 10, 20, and 40 μm diameter and a clear link between microhole diameter and switching time is seen. The 40 μm diameter microhole requires close to 1 s to switch, whereas smaller diodes are much faster (in agreement with the concentration polarisation mechanism). In applications the delay during switching is linked to losses in performance (and energy) and therefore fast ionic diodes are desirable, for example in desalination. Further work will be required to improve both speed (e.g. employing arrays of smaller microholes) and rectification ratio (improving porosity and structure).

Conclusions

In this communication we provide initial proof-of-concept evidence for current rectification and “ionic diode” phenomena in reconstituted cellulose materials without chemical surface modification. The ionic diode phenomenon for this single-material device is linked to space charge layer formation and concentration polarisation at the cellulose | aqueous electrolyte interface and strongly affected by ionic strength. Currently, the reported rectification effect relies on the inert PET microhole substrate material, which in future will have to be replaced by a different more sustainable inert material with an array of microholes. Further work will be directed towards controlling cellulose porosity, modifying charge within the films (by chemical modification or in composites), optimising microhole substrates, and modifying the polymer surface in contact to the aqueous phase. New devices based on cellulose ion rectifiers will be of considerable interest particularly in water purification and sensing and the new microhole diode mechanism will be very useful in device fabrication.

Acknowledgements

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Keywords: cellulose • desalination • ionic diode • rectification • voltammetry

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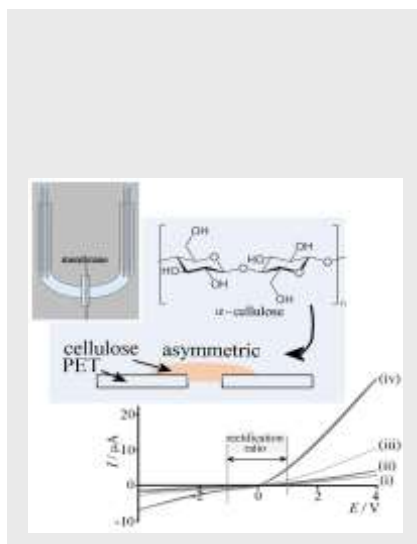
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Ionic Diodes Based on Regenerated α -Cellulose Films Deposited Asymmetrically onto a Microhole

Current rectification phenomena in aqueous NaCl are observed for cellulose films when immobilised onto a poly-ethylene-terephthalate substrate with microhole. The “open” state is dominated by ionic conductivity in cellulose whereas the “closed” state is caused by concentration polarisation.

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